Magnetic properties of the coupled ladder system MgV_2O_5

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We present magnetic susceptibility measurements on MgV_2O_5, a compound in which the vanadium oxide planes have the same topology as in CaV_2O_5. The most striking property is that there is an energy gap of about 15 K, much smaller than in CaV_2O_5, where the values reported are of the order of 500 K. We show that this may be understood naturally in terms of the phase diagram of the frustrated, coupled ladder system. This analysis leads to the prediction that MgV_2O_5 should have incommensurate dynamic spin fluctuations.

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The study of low dimensional, spin-1/2 magnets is a very active field of research. One of the recent successes has been the synthesis and theoretical understanding of spin ladder systems [1]. These consist of weakly interacting pairs of antiferromagnetic chains coupled by antiferromagnetic rungs, and the single most interesting result is the appearance of a gap in the spin excitation spectrum. The prototype of such systems is $SrCu_2O_3$, whose magnetic properties can be accounted for by a spin-1/2 Heisenberg model

$$H = \sum_{(i,j)} J_{ij} \vec{S}_i . \vec{S}_j \qquad (1)$$

restricted to the exchange integrals depicted in Fig. 1. In the case of $SrCu_2O_3$, it is believed that $|J_1| \ll J_2, J_2'$, so that the system is clearly in the ladder limit. The family of planar vanadates also contains compounds where V atoms in ionization state V^{4+} give rise to spin-1/2 planes having the topology of Fig. 1, and their primary difference from $SrCu_2O_3$ is that the coupling between the ladders is not a priori a small parameter. The first example in which a spin gap was reported is CaV_2O_5 [2]. The presence of a large spin gap (about 500 K) in spite of non-negligible inter-ladder coupling came as a surprise, and prompted four of the present authors to study the phase diagram of the model depicted in Fig. 1 [3]. In particular, they showed that the ladders behave in an essentially decoupled manner when the second-neighbor coupling constants J_2 and J_2' are large enough compared to J_1, and that there should be an ordered, incommensurate phase when the three coupling constants are comparable. These results provide a reasonable explanation of the presence of a large spin gap in CaV_2O_5 since, as we will argue below, the information currently available on the magnetic interaction parameters leads to the estimates $J_2/J_1 \simeq 3.5$ and $J_2'/J_1 \simeq 4.3$ for that system.

Materials which could be used to probe other regions of the rather rich phase diagram of Ref. [3] would be very welcome.

In this paper, we present magnetic susceptibility measurements for another member of the vanadate family with the same topology, namely MgV_2O_5. This system is quite intriguing because, although the vanadium oxide planes are very similar to those in CaV_2O_5 [4], the magnetic properties are strikingly different, with, in particular, a spin gap of only 15 K. As we shall argue below, this difference may be attributed to the presence of a helical ordered phase in the phase diagram of the model of Fig. 1, thus lending further support to the results of Ref. [3].

MgV_2O_5 was prepared by solid state reaction, starting from a mixture of MgO and VO_2, according to the procedure described in Ref. [5], and its structure was determined from x-ray powder diffraction Rietveld analysis [6]. It crystallizes in the orthorhombic system of space group Cmcm with, at 294 K, $a = 3.6913(2)$Å, $b = 9.9710(4)$Å, and $c = 11.0173(4)$Å. The structure retains the basic framework of the V_2O_5 host lattice, which is built up in one direction by infinite double lines of VO_5 square pyramids joined by alternate sharing of edges and corners to form vanadium zigzag chains along the a axis, and held together by corner sharing in the [001] direction. It is therefore indeed analogous to the structure of the compounds α'-NaV_2O_5 [7] and CaV_2O_5 [4]. A peculiar feature of the MgV_2O_5 structure is the shift by $a/2$ along [100] for alternate layers (doubling of the short inter-layer parameter), and the puckering of the V_2O_5 layers (angle $\mu = 21^o$) to accommodate Mg ions in tetrahedral coordination. An idealized view of the structure viewed down the a axis is presented in Fig. 2. As for CaV_2O_5, MgV_2O_5 is a monovalent (V^{4+}) oxide, and vanadium atoms are located on a single crystallographic

site.

Magnetic susceptibility measurements were performed using a superconducting quantum interference device QUANTUM DESIGN SQUID susceptometer. The magnetic field induction was 1kG. The molar susceptibility was corrected for diamagnetism by using Pascal's constants. The raw data are presented in Fig. 3. These data were reproduced on three different samples, with, however, a large variation of the temperature-independent background from sample to sample. The main features of these data are: i) a regular increase between 400 K and 100 K; ii) a small, not fully reproducible bump around 85 K; iii) a very slow decrease between 70 K and 15 K; iv) a much faster decrease down to 4 K; v) a very fast increase at lower temperature.

The low-temperature data are typical of a system with a spin gap. We have thus performed a fit of the data between 2 K and 25 K with the formula

$$\chi(T) = A + B/T + (C/\sqrt{T})\exp(-\Delta/T), \qquad (2)$$

where A includes all temperature-independent contributions (Van Vleck, plus possible contributions from impurity phases with temperature-independent susceptibility in this range), B/T accounts for paramagnetic impurities, and $(C/\sqrt{T})\exp(-\Delta/T)$ describes the susceptibility of a one-dimensional system with a gap [8]. The fit is depicted in the inset of Fig. 3, and the parameters used are $A = 1.71\,10^{-3}$ emu/mole, $B = 1.16\,10^{-3}$ emuK/mole, $C = 7.28\,10^{-3}$ emuK$^{1/2}$/mole and $\Delta = 14.8K$. The fit is very accurate, with a residue of only 1.6×10^{-6} over a temperature range 2 - 25 K. We have also tried to fit the data with a term of the form $C\exp(-\Delta/T)$ typical of gapped, two-dimensional systems [8]. The result was clearly not as good, which we take to indicate the effective one-dimensionality of the system, or that MgV_2O_5 remains in the limit of weakly interacting ladders.

While further investigation of this system, for example by Nuclear Magnetic Resonance, would be very useful to confirm these results, the presence of a rather small gap ($\simeq 15K$) as compared to CaV_2O_5 ($\simeq 500K$) is clearly very interesting. We believe that this result can be understood in terms of the model of Fig. 1, due to modest but not negligible differences in the structural parameters leading to important differences in the exchange integrals. The direct determination of exchange integrals for a particular system is a very difficult task, because it requires an accurate fit of the temperature-dependence of the susceptibility over a large temperature range. In vanadates this has been possible only in two cases for which we have a good theoretical understanding of the temperature-dependence of the susceptibility of the underlying model, α'-NaV_2O_5 [9,10] and CsV_2O_5 [11]. α'-NaV_2O_5 is a one-dimensional Heisenberg chain of corner-sharing VO_5 pyramids with a single exchange integral $J_2(NaV_2O_5)$. The susceptibility of this model is known very accurately from the work of many authors [12], and a fit of the experimental susceptibility

gives $J_2(NaV_2O_5) \simeq 530K$. CsV_2O_5 consists of weakly interacting pairs of edge-sharing pyramids. The relevant model is a Heisenberg model with only two spins coupled by an exchange integral $J_1(CsV_2O_5)$. The susceptibility can be calculated analytically, and a fit to the experimental results gave $J_1(CsV_2O_5) \simeq 146K$ [11].

To obtain estimates of the exchange integrals in other members of the family, we make the reasonable assumption that these depend only on the local geometry of the bonds. For corner-sharing pyramids (J_2,J'_2), the dominant process is superexchange, and the exchange integrals are expected to depend on the local parameters defined in Fig. 4 according to [9]

$$J_2(d,\theta), J'_2(d,\theta) \propto \cos^4(\theta)d^{-14}, \qquad (3)$$

where the exponent is given by empirical laws concerning the dependence of the overlap integrals on distance [13]. For edge–sharing pyramids (J_1), the origin of the interaction is not so clear. Assuming that it is due primarily to direct exchange between vanadium 3d orbitals, similar empirical laws predict that it should scale according to

$$J_1(d_{V-V}) \propto (d_{V-V})^{-10}. \qquad (4)$$

where d_{V-V} is the vanadium-vanadium distance. Having no other, more direct source of information at hand for vanadates, we will use these dependences in the following. The results for the exchange integrals of CaV_2O_5 and MgV_2O_5 based on the most accurate structural information available for α'-NaV_2O_5 [14], CsV_2O_5 [11], CaV_2O_5 [15] and MgV_2O_5 [6] are given in Table I. The trend is quite clear: J_1 is larger for MgV_2O_5 than for CaV_2O_5, while J'_2 is considerably smaller, so that the ratio J'_2/J_1 is approximately 4.3 for CaV_2O_5, but only 2.5 for MgV_2O_5. According to the analysis of the model performed in Ref. [3], this ratio is a very important parameter: $J'_2/J_1 = 4.3$ clearly puts CaV_2O_5 in the ladder limit with a large gap [16]. However, $J'_2/J_1 = 2.5$ with $J_2/J_1 = 2.8$ puts MgV_2O_5 very close to the helical ordered - hence gapless - phase according to the phase diagram obtained by Schwinger boson mean-field theory [3]. The system is thus expected to have a very small gap, as this vanishes continuously at the boundary. Of course, estimates based on Eqs. (3) and (4) are not very accurate [17], but the conclusions can be expected to remain qualitatively correct as long as the exchange integrals depend strongly on the distances, which has indeed been found to be the case in insulating oxides [18].

An interesting consequence of the proximity to a helical ordered phase is that MgV_2O_5 should exhibit incommensurate dynamic spin fluctuations. We do not present calculations to elaborate on this point here. This prediction could be verified by inelastic neutron scattering when single crystals of sufficient sizes become available.

Let us now turn to the high-temperature data. The increase of susceptibility with decreasing temperature, showing a maximum at intermediate temperatures, is

typical of systems with antiferromagnetic exchanges. Fitting the measured curve with a Heisenberg model has proven to be as difficult here as for other members of the family. The problem of the peak occurring well below the energy scale of the interactions may be due to poor theoretical estimates of the temperature dependence for frustrated systems with dynamic helical fluctuations. Work is in progress in this direction.

We focus finally on the broad susceptibility peak which occurs around 85 K. To address the possibility that this behavior is related to structural modifications, we have studied the thermal evolution of the x-ray diffractograms. X-ray powder patterns were collected up to $\theta = 30^o$ (except the diffractogram at 83 K which was collected up to 75° in order to perform a Rietveld refinement [6]) in a high-accuracy MICROCONTROLE diffractometer, using CuKα radiation (graphite monochromator) from an 18kW rotating-anode generator and a flowing cryostat with a stability range of 0.5 K. The thermal variation of the cell parameters, determined by least-squares refinement, is presented in Fig. 5. The lattice parameter a along the vanadium chains increases slightly from 170 K to 100 K, a temperature at which the fluctuations in the data suggest that a structural instability may be occurring, then decreases monotonically from 65 K to 8 K. Interestingly, the instability temperature range 100-65 K corresponds to the maximum observed in the susceptibility curve. Moreover, a shortening of the lattice parameter a is qualitatively consistent with an increase of the exchange integrals J_1 and J_2, hence with the experimental decrease of the susceptibility. However, it is difficult to correlate this with a structural modification because we did not observe a notable change on the Rietveld refinement of the structure performed at 83 K [6]. The interlayer distance b decreases continuously over the whole temperature range, while c presents no clear evolution. A structural determination at low temperatures (around 4 K) would be very useful, and we plan to perform this in the near future by neutron powder diffraction.

To summarize, the magnetic susceptibility data reported in this paper suggest that MgV_2O_5 is a new spin gap system with a gap of about 15 K. This very small value should be contrasted with the much larger value ($\simeq$500 K) reported for CaV_2O_5. We have shown that this difference can be understood in terms of the frustrated, coupled ladder system due to the proximity to an ordered helical phase in the case of MgV_2O_5. This interpretation suggests that MgV_2O_5 should have incommensurate dynamic spin fluctuations, a prediction which could be tested by inelastic neutron scattering as soon as suitably large crystals are available. Given the potential interest of systems with spin gaps in the range 0-30 K for studies under magnetic field, the magnetic properties of this system are likely to become a very active field of research.

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	d_{V-V}	J_1	$d_\perp$	$d(J_2)$	$d(J_2')$	J_2	J_2'	J_2/J_1	J_2'/J_1
CsV_2O_5	3.073	146							
α'-NaV_2O_5			0.698	1.962		530			
CaV_2O_5	3.0257	170	0.648	1.949	1.905	587	730	3.5	4.3
MgV_2O_5	2.976	201	0.666	1.954	1.975	565	511	2.8	2.5

TABLE I. Structural parameters and measured or estimated exchange integrals of CsV_2O_5, α'-NaV_2O_5, CaV_2O_5 and MgV_2O_5. Distances are in Å, and exchange integrals are in Kelvin.
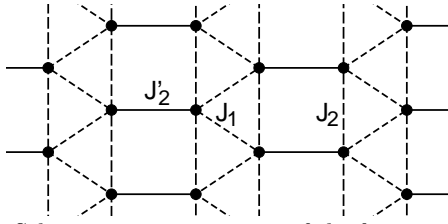
FIG. 1. Schematic representation of the frustrated coupled ladder system with one type of nearest neighbour exchange integral (J_1) and two types of next nearest neighbour exchange integrals (J_2,J_2')

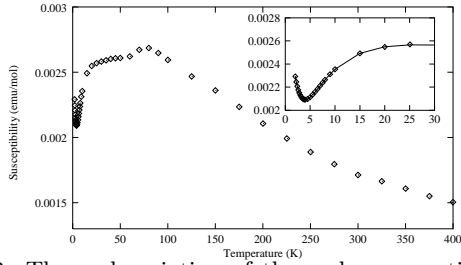FIG. 2. Idealized structure of MgV_2O_5 viewed down the a axis (3.69Å).

FIG. 3. Thermal variation of the molar magnetic susceptibility of MgV_2O_5. Diamonds: experimental points. Inset: enlargement of the low-temperature region with fit (solid line) to Eq. (2).

FIG. 4. a) V-$3d$ and O-$2p$ orbitals involved in superexchange between corner-sharing VO_5 square pyramids; b) basic parameters of the VO_5 square pyramid.

FIG. 5. Temperature dependence of lattice constants for MgV_2O_5. Triangles and black dots correspond to two successive collection sets. The open circles correspond to the Rietveld refinement at 83 K.